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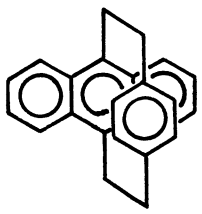
LAYERED COMPOUNDS. XII[1]. [2.2]PARACYCLO- AND [2.2](1,4)NAPHTHALENO-ANTHRACENOPHANES

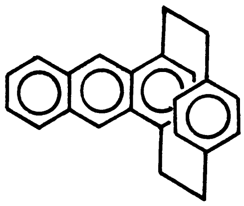
Akio IWAMA, Toshihiro TOYODA, Tetsuo OTSUBO, and Soichi MISUMI
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka 565

[2.2]Paracyclo-(9,10)- and -(1,4)-anthracenophanes (I and II) and [2.2](1,4)-naphthaleno(9,10)anthracenophane (III) have been synthesized and it is noted on the basis of their electronic spectra that in either paracyclo- or naphthaleno-anthracenophane, there is more appreciable transannular interaction in 9,10-bridged system than in 1,4-bridged one.

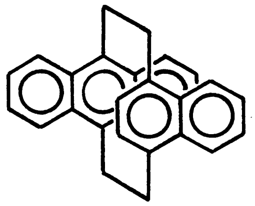
In the previous papers[1,2] of this series, we have reported the transannular electronic interactions in some layered anthracenophanes, particularly between two anthracene nuclei. For comparison of the properties of 9,10-bridged anthracenophanes with those of 1,4-bridged ones, this communication reports the synthesis and properties of [2.2]paracyclo-(9,10)anthracenophane (I) and -(1,4)anthracenophane (II), and [2.2](1,4)naphthaleno(9,10)anthracenophane (III). The synthesis of syn-[2.2](1,4)naphthaleno(1,4)anthracenophane (IV) has been reported in the preceding paper.[1]



I



II



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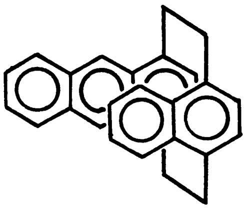
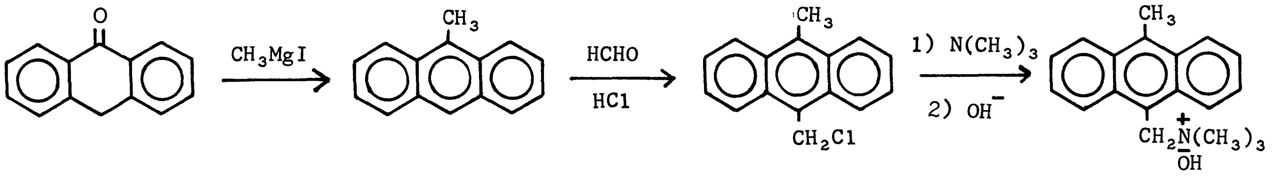
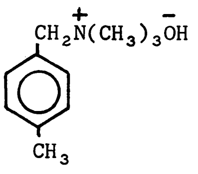


IV

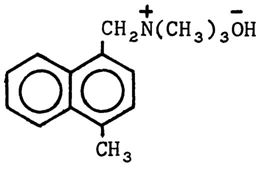
Cram[3] reported that paracyclo-anthracenophane I was not isolated in a pure state due to its instability, though it was obtained as a mixture with anti-[2.2](1,4)naphthalenophane by dehydrogenation of perhydro-compounds derived from [2.2]paracyclophane via several steps. By means of cross-breeding pyrolysis of two quaternary ammonium hydroxides (V and VI), however, we obtained the anthracenophane I as pure crystals. Thus, pyrolysis of an equimolar mixture of VI with V, which was synthesized from anthrone according to the scheme described below, followed by column chromatography of the resulting xylene filtrate on silica gel afforded a 26% yield of the desired anthracenophane I, yellow prisms from benzene [mp 168∼173°C (partly decomp.); Anal. Found: C, 93.51; H, 6.40. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54; mass m/e $308[M^+]$, 204, 104]. This compound was decomposed with color change to brown on prolonged standing at room temperature. Similarly, cross-breeding pyrolysis of a quaternary base VIII with an excess of VI gave [2.2]paracyclo(1,4)-anthracenophane (II) in a 1.6% yield, which was isolated by column chromatography on neutral alumina in a pure state, pale yellow needles from n-hexane-benzene (9:1) [mp 172.0∼173.5°C; Anal. Found: C, 93.23; H, 6.41. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54; mass m/e $308[M^+]$, 204, 104]. The naphthaleno-anthracenophane III was obtained in a 21% yield by pyrolysis of an equimolar mixture of V and VII in boiling xylene, filtration of the resulting warm xylene solution, and column chromatography on neutral alumina, successively, as light greenish yellow plates from benzene [mp 230.5∼231.5°C; Anal. Found: C, 93.99; H, 6.05. Calcd for $C_{28}H_{22}$: C, 93.80; H, 6.20; mass m/e $358[M^+]$,



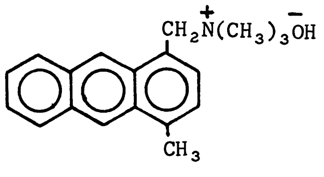
V



VI



VII



VIII

204, 154].

NMR spectral data of these anthracenophanes (I∼III) are depicted in Fig. 1. The spectrum of anthracenophane I having C_{2v} symmetry shows a singlet of benzene ring protons at higher field, typical A_2B_2 patterns of the other aromatic protons and methylene protons, respectively. In a case of isomeric anthracenophane II, Ha protons appear upfield and Hb protons downfield from the resonance position of the benzene protons in I due to a magnetic anisotropic effect caused by the anthracene nucleus. Therefore, meta-coupling is observed in the compound II. All the aromatic protons in naphthaleno-anthracenophane III are significantly shifted upfield compared to the corresponding ones in 9,10-dimethylanthracene and 1,4-dimethylnaphthalene and the aromatic protons in isomeric anthracenophane IV also show approximately same upfield shifts, suggesting that π-electron overlapping of two aromatic nuclei in compound IV is nearly as large as in compound III.

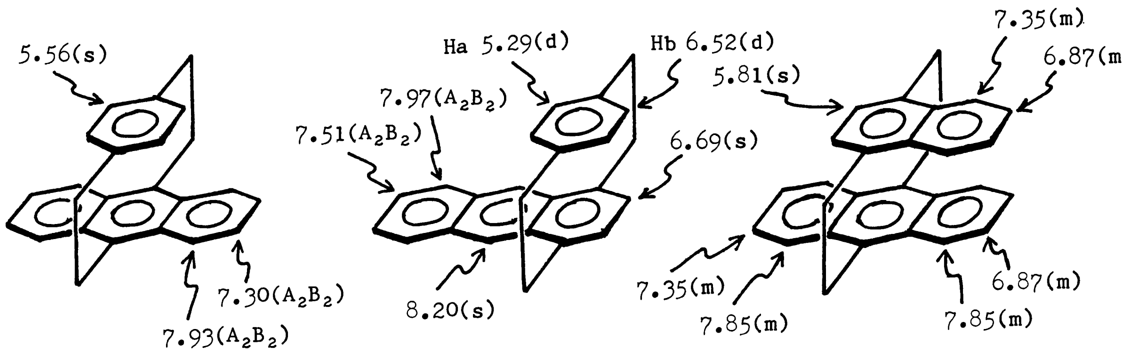


Fig. 1. NMR spectra (δ value) of three anthracenophanes (I∼III) in deuterochloroform.

The electronic spectra of two [2.2]paracyclo-anthracenophanes (I and II) and two [2.2](1,4)-naphthaleno-anthracenophanes (III and IV) are shown in Fig. 2. All the vibrational structure associated with the La band in anthracene become broad, especially in IV, and there are remarkable red shifts compared with 9,10- and 1,4-dimethylanthracenes, respectively. In either paracyclo- or naphthaleno-anthracenophane, the longest wavelength bands of 9,10-bridged one display more bathochromic shifts from the La band position of the corresponding dimethylanthracene than those of 1,4-bridged one, indicating that there is more transannular electronic interaction in the former system than in the latter.

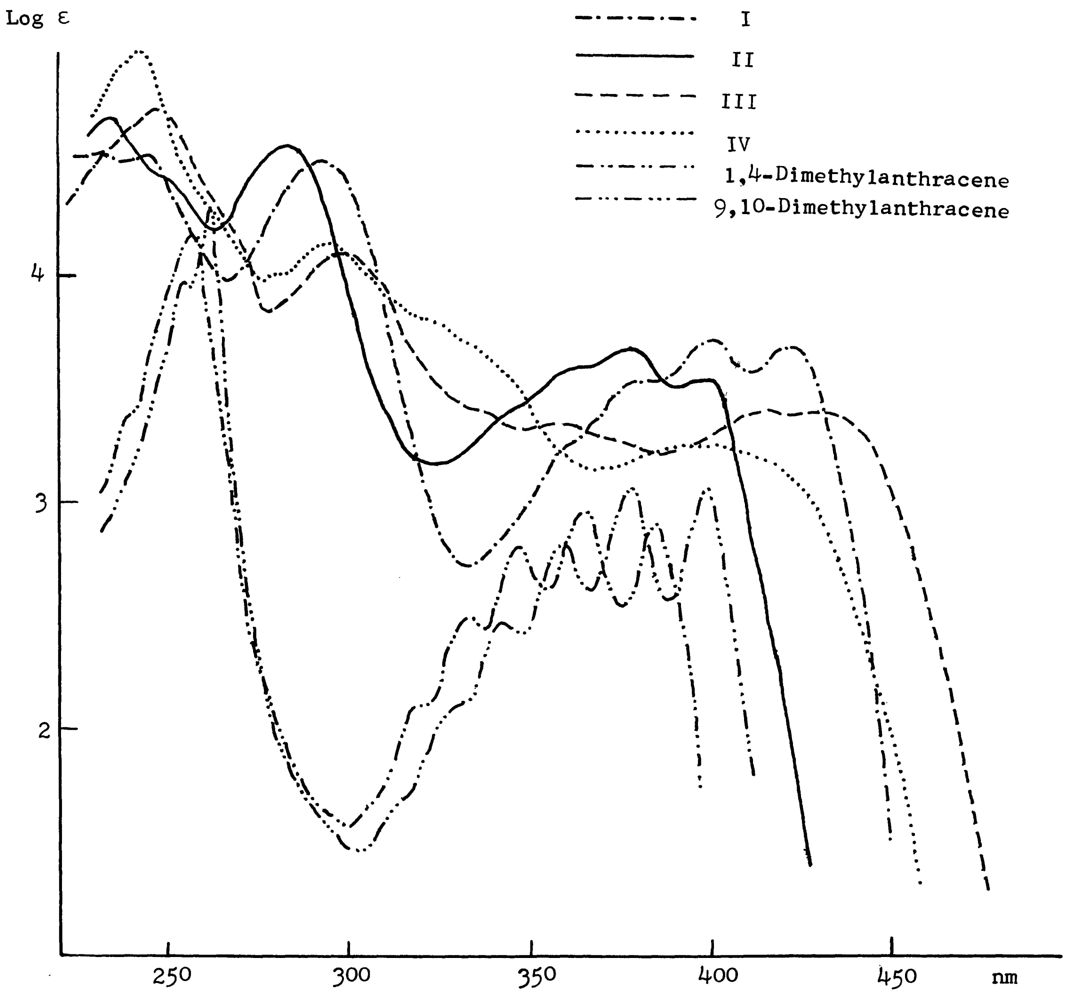


Fig. 2. The electronic spectra of four anthracenophanes (I~IV) and 1,4- and 9,10-dimethylanthracenes in tetrahydrofuran. The curves of two dimethylanthracenes are displaced downward by a log ε unit.

References

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2) T. Toyoda, I. Otsubo, T. Otsubo, Y. Sakata, and S. Misumi, ibid., 1972, 1731.

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